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Test Procedure for Uranium in Drinking Water Interlaboratory Collaborative Study

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16. ABSTRACT

An interlaboratory collaborative study was conducted to test a procedure selected for measurement of uranium in drinking water. Drinking water samples containing 8.1, 17.4, and 75.3 pCi/l were analyzed in triplicate by 18 participating laboratories.

The statistical analyses of the test results gave coefficients of variation for repeatability (within-laboratory precision) of 14.6, 8.1, and 8.3 percent for the three samples for an average repeatability precision of 10.3 percent over the uranium concentration range of 8 to 75 pCi/l. The analyses also gave coefficients of variation for reproducibility (combined within- and between-laboratory precision) of 15.3, 14.9, and 9.1 percent for an average reproducibility precision of 13.1 percent over the uranium concentration range of 8 to 75 pCi/l.

The accuracy indexes of the test procedure for the three uranium concentrations was 98.0, 102.6, and 101.9 percent for an average of 100.8 percent over the uranium concentrations range of 8 to 75 pCi/l.

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LIST OF ABBREVIATIONS AND SYMBOLS

ABBREVIATIONS

ASTM	-- The American Society for Testing and Materials
Cl^-	-- chloride
c/m	-- counts per minute
d/m	-- disintegrations per minute
DOE	-- The Department of Energy
EPA	-- Environmental Protection Agency
g/cm^3	-- grams per cubic centimeter
g/l	-- gram/liter
IAG	-- Interagency Agreement
kg	-- kilogram
MCL	-- maximum contaminant level
mg/l	-- milligram/liter
nCi/g	-- nanocurie/gram
NIPDWR	-- National Interim Primary Drinking Water Regulations
pCi/l	-- picocuries per liter
ppm	-- parts per million
µCi/g	-- microcurie/gram
2S %	-- Two sigma percent (two standard deviations in percent)

SYMBOLS

$A_j\%$	-- the accuracy index for the sample j level of uranium concentration
d_{ij}	-- the deviation of Lab i average from the grand average for sample j
$\%d_{ij}$	-- the percent deviation of Lab i average from the grand average for sample j
e_{ij}	-- the reduced deviation of Lab i average from the grand average for sample j
I_{r_j}	-- the repeatability interval for sample j level
I_{R_j}	-- the reproducibility interval for sample j level
k_{ij}	-- the ratio of Lab i average standard deviation (S_{ij}) to the pooled standard deviation (S_{r_j}) for sample j
n	-- the number of replicate analyses
P	-- the number of participants in the collaborative study
S_{ij}	-- the standard deviation of the replicate test results for sample j by Lab i
S_{L_j}	-- the standard deviation of between-laboratories precision for sample j

S_{r_j} -- the repeatability (within-laboratory) standard deviation for the sample j

$\bar{S}_{r_j}$ -- the smoothed repeatability standard deviation for sample j

S_{R_j} -- the reproducibility (combined within- and between-laboratory) standard deviation for sample j

$\bar{S}_{R_j}$ -- the smoothed reproducibility standard deviation for sample j

$S_{\bar{x}_j}$ -- the standard deviation of the grand average for sample j

t_c -- the critical value of the bias test for P participants

t_j -- the bias value for sample j

Tn -- the T-test value of the nth replicate, outlier test

U_j -- the adjusted within-laboratory standard deviation

$V_{L_j}\%$ -- the coefficient of variation for between-laboratories precision for sample j

$V_{r_j}\%$ -- the coefficient of variation for repeatability (within-laboratory) for sample j

$V_{R_j}\%$ -- the coefficient of variation for reproducibility (combined within- and between-laboratory) for sample j

X_h -- the test result of the replicate h

$\bar{X}_{ij}$ -- the arithmetic average of all replicate test results of sample j by Lab i

X_{ijh} -- the test result of replicate h of sample j by Lab i

$\bar{X}_j$ -- the grand average value for sample j

Y_j -- the known value of the sample j uranium concentration (pCi/l)

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INTRODUCTION

The National Interim Primary Drinking Water Regulations (NIPDWR) imply that when a gross alpha measurement of a drinking water sample exceeds 15 picocuries per liter (pCi/l), then an analysis for uranium should be done to determine the uranium alpha contribution to the gross alpha concentration. The method listed in the NIPDWR for the measurement of uranium in drinking water is a fluorometric method which determines uranium in mass units. It is now known (subsequent to the promulgation of the NIPDWR) that the ratio of uranium alpha activity to uranium mass concentration in ground water can vary significantly from that which is common to natural uranium ore deposits. Therefore, a test procedure for measuring total uranium alpha activity concentrations is needed that will more adequately relate to drinking water gross alpha activity. Such a test procedure was selected and tested in an interlaboratory collaborative study. This is a report of the results of that study.

The method of analysis used in this study is a simplified version of a method that measures the uranium isotopic concentrations in the sample by alpha spectrometry. This method measures total uranium alpha activity, the measurement needed for a gross alpha assessment of a drinking water sample. This method is included in the updated EPA procedures manual, EPA-600/4-80-032, August 1980, "Prescribed Procedures for Measurement of Radioactivity in Drinking Water".

The purpose of the collaborative study of the selected test procedure is to determine what precision and accuracy can be expected by the use of the procedure by any competent laboratory in the analysis of drinking water samples for alpha activity contributed by the uranium in the water samples.

CONCLUSIONS

The repeatability precision (within-laboratory precision), reproducibility precision (the combined within- and between-laboratory precision), and the accuracy have been determined for the test procedure by a multilaboratory test in this study, and they hereby become criteria by which to evaluate an alternate test procedure for equivalency.

The estimated repeatability (within-laboratory), single-operator, single machine, same-day, relative precision of the test procedure for the determination of total uranium alpha concentrations at the 8.1 pCi/l level (averaged over the 18 participants) is ±2.3 pCi/l (28.4%, 2S%); at the 17.4 pCi/l level (averaged over the 17 participants) is ±2.9 pCi/l (16.5%, 2S%); and at the 75.3 pCi/l level (averaged over the 18 participants) is ±12.8 pCi/l (17.0%, 2S%), for an average 2S percent of 20.6 percent for the range of uranium alpha concentrations of 8 to 75 pCi/l.

The estimated reproducibility (combined within- and between-laboratory), multi-operator (multilaboratory), single-machine, same-day, relative precision of the test procedure in the determination of total uranium alpha concentrations at the 8.1 pCi/l level (averaged over the 18 participants) is ±2.4 pCi/l (29.6%, 2S%); at the 17.4 pCi/l level (averaged over the 17 participants) is ±5.3 pCi/l (30.4%, 2S%); and at the 75.3 pCi/l level (averaged over the 18 participants) is ±14.0 pCi/l (18.5%, 2S%); for an average 2S% of 26.2 percent for the range of uranium alpha concentrations of 8 to 75 pCi/l.

In terms of the 95 percent repeatability interval (on the basis of test error alone) the difference in absolute value, of two test results obtained in the same laboratory at the 8.1 pCi/l level of uranium alpha concentration can be expected to exceed 2.3 pCi/l only 5 percent of the time; at the 17.4 pCi/l level, 5.2 pCi/l only 5 percent of the time; and at the 75.3 pCi/l level, 22.4 pCi/l only 5 percent of the time. These average to be 29.3 percent of the uranium alpha concentration over the range of 8 to 75 pCi/l. When differences exceed 29.3 percent of the concentration, then one or both of the test results are suspect.

In terms of the 95 percent reproducibility interval (on the basis of test error alone), the difference, in absolute value, of two test results obtained in different laboratories at the 8.1 pCi/l level of uranium alpha concentration can be expected to exceed 2.9 pCi/l only 5 percent of the time; at the 17.4 pCi/l level, 6.6 pCi/l only 5 percent of the time; and at the 75.3 pCi/l level, 28.5 pCi/l only 5 percent of the time. These average to be 37.2

percent of the uranium alpha concentration over the range 8 to 75 pCi/l. When differences exceed the 37.2 percent of the uranium alpha concentration, then one or both test results are suspect.

The accuracy of the test procedure expressed as the accuracy index in percent for the three uranium alpha concentration levels are 98.0, 102.6, and 101.9 percent respectively, for an average accuracy index of 100.8 percent over the range of concentrations of 8 to 75 pCi/l.

The sensitivity of the test procedure is not limited as much by the chemistry of the procedure as it is by the background and the counting efficiency of the alpha counting system used. With a 1-liter sample, an alpha background of 0.1 cpm, a counting time of 100 minutes, and a counting efficiency of 15 percent (0.15 cpm/dpm), the sensitivity of the test procedure for uranium alpha would be about 0.3 pCi/l at the 95 percent confidence level (using sensitivity as defined in the NIPDWR).

The lack of an adequate carrier with which to determine chemical recovery in each sample analyzed, and having to use a predetermined recovery factor, causes some uncertainty in the adjusted test results (adjusted by recovery factor). However, the predetermined recoveries averaged for the 18 laboratories was 91. ± 15. percent, indicating a relatively high chemical recovery for the test procedure and therefore minimal uncertainty in the adjusted test results.

The t-test to show significant differences and method bias showed that the test procedure did not contain significant systematic errors and therefore no bias was indicated for uranium alpha concentrations up to 75 pCi/l.

RECOMMENDATIONS

It is recommended that the test procedure used in this study (described in detail in Appendix B) be used to monitor drinking water samples for uranium alpha contribution to the gross alpha activity when the gross alpha activity exceeds the amount specified in the NIPDWR (15 pCi/l, Section 141.15).

It is recommended that a change be made in the preparation of the separated uranium fraction for counting the alpha activity. It is also recommended that the change be verified experimentally to demonstrate the benefit to the Test Procedure before the change is incorporated into the Test Procedure. To make that change in the preparation of the separated uranium fraction for alpha counting, the following changes and additions to the Test Procedure (Method 908.0) are proposed. Replace existing steps 8.2.5 through 8.2.9 with the following 8.2.5 through 8.2.10 steps.

8.2.5 Elute the uranium with six column volumes of 0.1N HCl, collecting the eluate in a 150 ml beaker.

8.2.6 Evaporate the eluate to near dryness, then add 1 ml 12N HCl (conc.), 10 ml of water, 0.2 ml 20% $TiCl_3$, and 1 ml of lanthanum carrier solution, stir.

8.2.7 Add 0.5 ml HF (conc.), stir well and allow to stand for 30 minutes.

8.2.8 Filter through 47 mm, 0.2 µm pore membrane filter, collecting the coprecipitated U/LaF_3.

8.2.9 Wash the U/LaF_3 with 10 ml of water followed by 10 ml of ethanol.

8.2.10 Air dry the filter for at least 1 hour before counting for alpha activity.

Also add the following item to the "Apparatus" section of the procedure.

5.7 0.2 µm pore, 47 mm diameter membrane filter that withstand the acid treatment in the Test Procedure and will lay flat after drying (such as Gelman AN-200).

And add the following items to the "Reagents" section of the procedure.

6.15 Lanthanum nitrate, (1.0 mg La^{+3}/ml). Disolve 3.11 g $La(NO_3)_3 \cdot 6H_2O$ in one liter of 0.1N HNO_3.

6.16 Hydrofluoric acid, 29N : HF (conc.) sp. gr. 1.18, 49%.

6.17 Titanium trichloride, $TiCl_3$: 20%

The term "column volume" in the test procedure should be clarified. This can be done by simply giving the milliliters of the resin bed volume specified in the procedure. A resin bed 1.3 cm in diameter by 8.0 cm high will have a volume of 10.6 ml. Then in Section 8.2.3 of the procedure, after the expression "-- with 6 column volumes", put in parentheses (6 x 10.6 ml = 63.6 ml, or 65. ml, rounded to the nearest 5 ml).

Since no carrier or tracer is used in the procedure with each sample to determine chemical recovery, it is recommended that with each set of samples to be analyzed by this test procedure, a spiked sample (to determine recovery) and a sample duplicate (to verify precision) be analyzed. This recommendation should be incorporated into the procedure.

EXPERIMENTAL PROCEDURES

ANALYTICAL TEST PROCEDURE

The analytical test procedure used in this study is described in detail in Appendix B. The procedure is capable of quantifying all uranium alpha emitting isotopes in drinking water.

COLLABORATIVE TEST PROCEDURES

Uranium Standard Solution Preparation

An ampoule of uranium standard solution, prepared by the National Bureau of Standards, was sent to each participant for recovery and counting efficiency determinations. That solution had a total uranium (U-238, U-235, and U-234) alpha specific activity of 5,171 dpm/g.

Uranium Concentrate Preparation

Three uranium concentrates were prepared for the collaborative study. The concentrates were prepared by dilution of a standard uranium solution of natural isotopic composition prepared by the National Bureau of Standards (NBS) for the Quality Assurance Division, U.S. Environmental Protection Agency, Las Vegas, Nevada. The standard solution was one molar in nitric acid. The calculated isotopic uranium radioactivity concentrations on November 1978, as specified by the National Bureau of Standards, were uranium-234, 2,478 ± 129 disintegrations per minute per gram (dpm/g); uranium-235, 119 ± 0.5 dpm/g, and uranium-238, 2,574 ± 8 dpm/g.

Uranium concentrate #1 was prepared by delivering 0.6910 g of the NBS stock solution to a tared 1,000-milliliter volumetric flask and diluting to 1 liter with 0.5 M HCl. The final weight of the solution was 1,005.4 grams and the uranium concentration was calculated to be 3.55 ± 0.19 dpm/g. The specific gravity of the solution was 1.0067 g/ml at 22.2°C based on the average of two determinations using a calibrated pycnometer. The concentration of the solution was then calculated to be 3.58 ± 0.19 dpm/ml. A 5-milliliter sample of this solution diluted to 1 liter with uranium-free water is equivalent to a total uranium concentration of 8.1 ± 0.4 pCi/l. After complete mixing of the solution, approximately 20 ml portions were sealed in 25 ml glass ampoules labeled uranium concentrate #1 and sent to the participants for analysis. Uranium concentrates #2 and #3 were prepared in the same manner as uranium concentrate #1 and data relative to all three concentrates are shown as follows:

Uranium Concentrate	Weight of NBS Standard Standard (g)	Total Weight of 0.5 M HCl Solution (g)	Conc. (dpm/g)	Specific Gravity (g/ml)	Conc. (dpm/ml)	Conc. When Diluted* (pCi/l)
#1	0.6910	1005.4	3.55 ± 0.19	1.0067	3.58 ± 0.19	8.1 ± 0.4
#2	1.4924	1005.1	7.68 ± 0.40	1.0068	7.73 ± 0.40	17.4 ± 0.9
#3	6.4559	1005.3	33.2 ± 1.7	1.0072	33.4 ± 1.7	75.3 ± 3.9

*5 ml of the concentrate diluted to 1 liter.

The concentrations of the three uranium concentrates were verified by alpha pulse-height analysis comparisons to a uranium-232 standard which had been previously calibrated with NBS standardized uranium-236. A 1-milliliter aliquot of uranium-232 standard solution was added to a 1-milliliter sample of each concentrate. These solutions were mixed, made 8 molar in hydrochloric acid, and passed through AG1-X4 anion exchange resin to remove daughter activities which were present. The uranium was eluted with 0.1 M HCl and electrodeposited on a 0.75-inch diameter stainless steel disk for alpha pulse-height analysis (APHA) spectrometry. By comparing the net count rate of the uranium-232 to the net count rates of uranium-234, -235, and -238, the concentrations of the uranium concentrates were determined. The values of the concentrates fell within the error limits as derived from the errors specified by the NBS for the standard solution. The following data summarizes the results of this verification.

Uranium Concentrate	Known Concentration Calculated From Dilution of NBS Standard (dpm/ml)	Concentration Measured by APHA (dpm/ml)*	% Difference From Known Value
#1	3.58 ± 0.19	3.57 ± 0.12	0.3
#2	7.73 ± 0.40	7.62 ± 0.19	1.4
#3	33.4 ± 1.7	34.4 ± 3.4	3.0

*Errors are one sigma counting errors only.

General Procedures

A total of 25 laboratories agreed to participate in the collaborative study and 19 laboratories submitted their results. All laboratories who submitted results are listed in Appendix A. All laboratories were supplied with the proposed EPA procedure for the analysis of total uranium alpha activity in drinking water (Appendix B), a Data Sheet (Appendix C), a Collaborative Study Instruction Sheet (Appendix D), a Questionnaire (Appendix E), and three unknown reference samples labeled uranium concentrate 1, 2, and 3.

By diluting a 5-milliliter aliquot of each concentrate to 1 liter with the participant's drinking water, the concentrations of the reference samples were calculated to be 8.1, 17.4 and 75.3 pCi/l total uranium alpha activity.

Each participating laboratory was requested to perform triplicate analyses of a 1-liter sample of their drinking water to determine a blank value. The authors believed that some of the participants might have had a high drinking water blank and therefore bias the reference values. A blank value for this study was therefore defined as the counts per minute of 1 liter of the participant's drinking water including counter background.

The results of each laboratory were reported on a data sheet which specified sample identification, volume, gross counts, counting time, counter background, total uranium alpha activity in pCi/l, average recovery factor (R), and average counting efficiency (E). All calculated data were checked at Mound Facility, and any significant differences between the calculated and reported values were resolved with the individual participants.

DATA PROCESSING PROCEDURES

The data from the 19 participants were tested for outliers by the ASTM recommended criterion for rejection (ASTM 1980). For this rejection criterion, with n observations listed in order of increasing value by $x_1 \leq x_2 \leq x_3 \leq \ldots \leq x_n$, if the outlying values x_n or x_1 are in question, then T_n or T_1 were calculated as follows:

$$T_n = (x_n - \bar{x})/s \qquad (1)$$

$$T_1 = (x_1 - \bar{x})/s$$

where: T_n; T_1 = test criterion

$\bar{x}$ = arithmetic average of all n values

s = the estimate of the population standard deviation based on the sample data

If T_n or T_1 values exceeded the critical value, the measurement in question was rejected. Critical values of T for a 5 percent two-sided level of significance were used for the rejection criterion.

A statistical evaluation of the test results was carried out by the procedures described in E-691, E-177, and E-178 of the ASTM Standard Part 41, 1980. The standard deviations and other statistical parameters, and equations for their calculations are listed below. The standard deviation of individual participant (or laboratory) test results, S_{ij}, was determined by Equation 2.

$$S_{ij} = \left[\sum_{h=1}^{n_{ij}} (X_{ijh} - \bar{X}_{ij})^2 / (n_{ij} - 1) \right]^{1/2} \qquad (2)$$

where: X_{ijh} = the result reported for the h replicate of the j sample material by Lab i

$\bar{X}_{ij}$ = the mean of the individual results for sample j for Lab i

n_{ij} = the number of replicates reported for sample j by Lab i

The repeatability (within-laboratory) standard deviation, S_{r_j}, for each sample was determined by Equation 3 and 3A.

Where the number of replicates was the same (3) for all participants, Equation 3 was used.

$$S_{r_j} = \left(1/P \sum_{i=1}^{P} S_{ij}^2 \right)^{1/2} \qquad (3)$$

where: P = the number of participants in the study.

Where the number of replicates were not the same for all participants, Equation 3A was used.

$$S_{r_j} = \left(\frac{\sum_{i=1}^{P} [(n_{ij} - 1)\, S_{ij}^2]}{\sum_{i=1}^{P} (n_{ij} - 1)} \right)^{1/2} \qquad (3A)$$

The standard deviation of the grand average for each sample, $S_{\bar{X}_j}$, was determined by Equation 4.

$$S_{\bar{X}_j} = \left[\sum_{i=1}^{P} (\bar{X}_{ij} - \bar{X}_j)^2/(P-1) \right]^{1/2} \quad (4)$$

where: $\bar{X}_{ij}$ = the average of the test results for sample material j by Lab i

$\bar{X}_j$ = the grand average for sample material j

The standard deviation of between-laboratories precision for each sample material, S_{L_j}, was determined by Equation 5.

$$S_{L_j} = \left(S_{\bar{X}j}^2 - S_{r_j}^2/n \right)^{1/2} \quad (5)$$

The reproducibility (combined within- and between-laboratory) standard deviation for each sample, S_{R_j}, was determined by Equation 6.

$$S_{R_j} = (S_{r_j}^2 + S_{L_j}^2)^{1/2} \quad (6)$$

The deviation of laboratory averages from the grand average for each sample, d_{ij}, was determined by Equation 7.

$$d_{ij} = \bar{X}_{ij} - \bar{X}_j \quad (7)$$

The percent deviation of laboratory averages from the grand average for each sample, % d_{ij}, was determined by Equation 8.

$$\% \, d_{ij} = 100 \, (d_{ij}/\bar{X}_j) \quad (8)$$

The estimated standard error of a cell average, calculated on the basis of replication error only, U_j, for sample #1, is determined by Equation 9.

$$U_j = S_{r_j} [(P-1)/nP]^{1/2} \quad (9)$$

For samples #2 and #3, duplicate analyses were made by one lab. Thus for samples #2 and #3 the nP value (total replicates) in Equation 9 was replaced by $\sum_{i=1}^{P} n_{ij}$

Reduced deviations (e_{ij}) for each participant for each sample were determined by Equation 10.

$$e_{ij} = d_{ij}/U_j \tag{10}$$

The ratio (k_{ij}) of the standard deviation of participant replicate analyses (S_{ij}) to the pooled standard deviation (S_{r_j}) for each sample was determined by Equation 11.

$$k_{ij} = S_{ij}/S_{r_j} \tag{11}$$

The coefficient of variation for repeatability (within-laboratory) for each sample, $V_{r_j}\%$, was determined by Equation 12.

$$V_{r_j}\% = 100\ S_{r_j}/\bar{X}_j \tag{12}$$

The coefficient of variation for between-laboratories precision for each sample, $V_{L_j}\%$, was determined by Equation 13.

$$V_{L_j}\% = 100\ S_{L_j}/\bar{X}_j \tag{13}$$

The coefficient of variation for reproducibility (combined within- and between laboratory) for each sample, $V_{R_j}\%$, was determined by Equation 14.

$$V_{R_j}\% = 100\ S_{R_j}/\bar{X}_j \tag{14}$$

Smoothed values of the repeatability and reproducibility standard deviations for each sample, $\bar{S}_{r_j}$ and $\bar{S}_{R_j}$ were determined by Equations 15 and 16, respectively.

$$\bar{S}_{r_j} = (\bar{V}_r\%)(\bar{X}_j)/100 \tag{15}$$

$$\bar{S}_{R_j} = (\bar{V}_R\%)\bar{X}_j/100 \tag{16}$$

Where $\bar{V}_{r\%}$ = average of $V_{r_j\%}$ for the 3 samples

$\bar{V}_{R\%}$ = average of $V_{R_j\%}$ for the 3 samples

Assuming that the test errors are normally distributed and using a 95 percent probability level, the 95 percent repeatability interval (I_{r_j}) and the 95 percent reproducibility interval (I_{R_j}) for each sample were determined using the smoothed standard deviations in Equations 17 and 18, respectively.

$$I_{r_j} = 2(2)^{1/2}\,\bar{S}_{r_j} = 2.83\,\bar{S}_{r_j} \tag{17}$$

$$I_{R_j} = 2(2)^{1/2}\,\bar{S}_{r_j} = 2.83\,\bar{S}_{r_j} \tag{18}$$

The accuracy index ($A_j\%$) a percent relationship of the grand average ($\bar{X}_j$) to the known value (Y_j) for each sample material was determined by Equation 19.

$$A_j\% = 100\,\bar{X}_j/Y_j \tag{19}$$

A comparison of the grand average value ($\bar{X}_j$) with the known value (Y_j) for each sample in a bias test was determined by Equation 20 (Youden and Steiner, 1975).

$$t_j = \frac{\bar{X}_j - Y_j}{S_{\bar{x}_j}/(P)^{1/2}} \text{ , } (P-1) \text{ degrees of freedom} \tag{20}$$

where t_j = the bias test result for the j sample

P = the number of participants

RESULTS AND DISCUSSION

For this collaborative study of the selected test procedure (Appendix B), uranium in water concentrate solution batches were prepared and a portion was sent to each participant. Three separate batches were prepared with three different uranium concentrations. Concentrates were used so that participants would make specified dilutions with their own drinking water, thereby subjecting the test procedure to 19 different drinking water sources.

The test results from the 19 participants for the three uranium concentrations in drinking water are tabulated in Table 1. The participants are identified by randomly assigned laboratory numbers. Table 1 also lists the counting error (1 sigma, S_u) associated with each test result. The recovery data in Table 1 is a listing of the three (and sometimes four) replicate uranium analyses of spiked (with standard uranium) samples by the test procedure by each laboratory for the purpose of recovery determination. The recovery factor (average of the replicate tests) was used to correct analytical results of the three test samples.

The test results of Lab 12 for Sample 2 and Lab 20 for samples 1 and 3 failed the laboratory outlier test at the 5 percent significance level (ASTM, E-178, 1980) and were therefore rejected (not used in the precision and accuracy calculations). The test results of Lab 20 for Sample 2 did not fail the outlier test but was found to be significantly different from the grand average by the t-test for significant differences (Youden and Steiner, 1975) and was therefore rejected (not used in the precision and accuracy calculations).

Table 2 gives the known value (Y_j) and grand average ($\bar{\bar{X}}_j$) for each sample and the following precision parameters.

$S_{\bar{\bar{X}}_j}$, the standard deviation of the grand average for the j sample

S_{r_j}, the pooled standard deviation (within-laboratory) for the j sample

S_{L_j}, the square root of the component of variance between-laboratories, $S_{L_j}^2$, for the j sample

S_{R_j}, an estimate of the between-laboratories precision, a combined within- and between-laboratory precision, or reproducibility precision for the j sample

$V_{r_j}\%$, the coefficient of variation for repeatability, or the estimated relative standard deviation for within-laboratory precision, or repeatability index for the j sample

$V_{L_j}\%$, the coefficient of variation for between-laboratories precision for the j sample

$V_{R_j}\%$, the coefficient of variation for reproducibility, the percent coefficient of variation for the total variability of a single test result including both within- and between-laboratory variability, or reproducibility index for the j sample

$\bar{S}_{r_j}$, the smoothed value of S_{r_j}

$\bar{S}_{R_j}$, the smoothed value of S_{R_j}

I_{r_j}, the repeatability interval--the maximum permissible difference due to test error between two test results obtained in a single laboratory (or by a single participant) at the j sample level

I_{R_j}, the reproducibility interval--the maximum permissible difference due to test error and systematic error between two test results obtained in two different laboratories at the j sample level

Table 3 lists, by participant, the average and the standard deviation of the participant test results for each of the three sample materials (cells). Table 3 also lists the S_{r_j} and an adjusted S_{r_j} value designated by U_j for for each sample material.

Table 4 lists, by participant, the deviation and the percent deviation of the participant average from the grand average for each sample material and the standard deviation of the grand average for each sample material, $S_{\bar{x}_j}$.

Table 5 lists, by participant, the reduced deviations (e_j) for each sample material.

Table 6 lists, by participant, the ratio (k_j) of the participant test results standard deviation (S_{ij}) to the pooled standard deviation (S_{r_j}) for each sample material. This table points out potential outliers. Sample 1 for Participant 8, Sample 2 for Participant 2, and Sample 3 for Participant 14, show ratio values higher than the critical value for 17 or 18 participants and 3 replicates (2.06). Since the average of those participant and sample test results were not significantly different from the respective grand average, those test results were not rejected.

For each of the three sample materials, Table 7 lists the known value (Y_j, pCi/l); the grand average, ($\bar{\bar{x}}_j$, pCi/l); the accuracy index, (A_j, %); the standard deviation of the grand average, ($S_{\bar{x}_j}$, pCi/l); the bias value, (t_j); the critical value for significance for 17 and 18 participants, (t_c); and the number of participants in the study, (P_j). The table also

shows the average accuracy index for the test procedure (100.8%). Table 7 shows no bias in the test procedure for the range of uranium concentrations tested (8 to 75 pCi/l).

The average of the recoveries for the 18 participants is 91 ± 15 percent, indicating that the chemistry of the test procedure is quite accurate and reliable.

From Table 2 it can be seen that the standard deviations (S_{rj}, S_{Lj}, and S_{Rj}) depend on the level of uranium concentration. However, the percent coefficients of variation as calculated from those standard deviations (V_{rj} %, V_{Lj} %, and V_{Rj} %) show a rather fixed percent relationship to all three levels of uranium concentration.

The repeatability (within-laboratory) and reproducibility (total between-laboratory) intervals (I_{rj} and I_{Rj}) for each sample material were calculated with smoothed S_{rj} and S_{Rj} values ($\bar{S}_{rj}$ and $\bar{S}_{Rj}$, respectively). The values listed in Table 2 were calculated at the 95 percent probability level and are thereby designated as the 95 percent repeatability and 95 percent reproducibility intervals. The 95 percent repeatability interval is that difference value based on test error alone between two test results obtained by the same participant (or laboratory) that would be exceeded only about 5 percent of the time. The 95 percent reproducibility interval is that difference value between two test results obtained by two different participants (or laboratories) that would be exceeded only about 5 percent of the time. When difference values exceed the interval values, one or both test results are suspect. The study shows the estimated average 95 percent repeatability interval to be 29.3 percent of the uranium concentration level over the range of 8 to 75 pCi/l. The estimated average 95 percent reproducibility interval is shown to be 37.2 percent over the same uranium concentration range. It should be realized that those interval values are based on a limited 18 participant average.

In the questionnaire sent to all of the participants in the study, Question 5 asked, "Do you believe that this would be a good reference method for uranium in drinking water?" Fifteen participants answered "yes", two said "no", and two were undecided. Appendix E is a summary of responses to the questionnaire.

Appendix F is a listing of the comments made by the participants about the test procedure. Responses to Questions 2, 5, 6, and 7 are addressed in the Recommendations section of this report. In response to Question 3 one participant commented that the method of transfer of the uranium eluant from the beaker to the counting planchet was questionable. Such transfers are made in many radiochemical methods and should not cause serious problems. In response to Question 4 one participant suggested that new ion exchange resin should be specified for each analysis rather than regenerating the resin. This can and should be done if the analyst does not have confidence in the regenerating procedure. The regenerating procedure should completely regenerate the resin from drinking water levels of uranium concentrations. Re-use of the resin is not recommended if high levels of uranium concentration (>500 pCi/l) have been put through the resin bed. In response to Question 10

one participant commented that the uranium yields would vary with the dissolved solids in the water sample. High carbonate content is usually associated with high dissolved solids and carbonate does complex uranium and tends to prevent its hydroxide precipitation. The test procedure addresses this problem adequately. The 19 different water supplies used in this collaborative study suggest that uranium yield is not tied to the dissolved solids content when this test procedure is followed.

TABLE 1. URANIUM IN DRINKING WATER, REPLICATE ANALYSES DATA

Lab	Sample Uranium Concentration, (counting error), [a] pCi/l			Recovery [b] Percent
	1	2	3	
1	8.67 (0.335)	22.76 (0.537)	93.03 (1.081)	81.43
	9.42 (0.349)	22.51 (0.534)	84.07 (1.027)	76.23
	9.18 (0.345)	19.57 (0.499)	75.21 (0.972)	91.08
2	10.46 (0.641)	25.01 (0.981)	92.06 (1.872)	78.2
	7.85 (0.558)	19.94 (0.877)	74.13 (1.680)	69.1
	7.69 (0.553)	18.72 (0.851)	86.83 (1.818)	80.0
3	7.02 (0.432)	13.66 (0.587)	83.88 (1.418)	101.0
	7.69 (0.450)	13.33 (0.580)	75.37 (1.345)	97.3
	7.97 (0.458)	12.05 (0.553)	76.86 (1.358)	106.0
4	9.12 (0.809)	14.62 (1.016)	73.38 (2.252)	82.5
	8.23 (0.771)	15.44 (1.043)	76.47 (2.298)	79.5
	8.02 (0.761)	(15.0)	(74.9)	
5	8.17 (0.298)	17.61 (0.432)	74.39 (1.242)	102.5
	7.89 (0.293)	15.59 (0.407)	79.29 (1.282)	97.6
	7.62 (0.288)	17.18 (0.426)	75.48 (1.251)	96.1
7	6.13 (0.367)	17.71 (0.681)	74.84 (1.133)	83.0
	6.40 (0.373)	18.52 (0.690)	82.85 (1.183)	83.0
	7.11 (0.388)	18.86 (0.693)	73.72 (1.126)	89.9
8	3.97 (0.888)	21.05 (1.800)	64.98 (3.090)	45.0
	11.01 (1.341)	21.92 (1.834)	75.32 (3.321)	36.0
	8.28 (1.186)	22.92 (1.873)	80.48 (3.431)	41.0
9	8.31 (0.742)	17.22 (1.043)	76.60 (2.160)	115.5
	7.05 (0.689)	18.73 (1.086)	69.25 (2.055)	104.9
	7.17 (0.694)	16.68 (1.027)	71.24 (2.083)	108.3
10	9.22 (0.602)	17.88 (0.833)	70.16 (1.642)	99.0
	8.87 (0.591)	17.49 (0.824)	72.65 (1.671)	96.0
	8.95 (0.594)	17.53 (0.825)	66.52 (1.599)	99.0

(continued)

See footnotes at end of table, page 18.

TABLE 1. (Continued)

Lab	Sample Uranium Concentration, (counting error), [a] pCi/l			Recovery [b] Percent
	1	2	3	
11	8.16 (0.525)	14.67 (0.691)	83.22 (1.614)	96.9
	6.76 (0.482)	17.05 (0.743)	88.80 (1.666)	92.6
	7.41 (0.503)	15.72 (0.715)	65.67 (1.435)	102.9
12	8.38 (0.239)	2.79 (0.148) [d]	76.84 (0.696)	91.6
	7.70 (0.230)	3.23 (0.157) [d]	77.85 (0.701)	90.3
	6.78 (0.217)	3.14 (0.156) [d]	77.35 (0.699)	89.9
14	7.54 (0.721)	17.57 (1.032)	81.61 (2.130)	77.6
	8.46 (0.755)	16.21 (0.995)	92.51 (2.265)	82.9
				109.0
	8.84 (0.769)	19.41 (1.079)	64.37 (1.898)	129.0
18	6.97 (0.662)	18.83 (1.018)	73.28 (1.946)	95.3
	9.11 (1.141)	17.82 (1.550)	80.15 (3.206)	81.3
	7.12 (0.668)	20.09 (1.640)	78.64 (3.176)	97.2
20	5.29 (0.348) [e]	11.96 (0.518) [e]	56.64 (1.122) [d]	109.6
	4.33 (0.316) [e]	12.20 (0.524) [e]	-	106.0
	5.47 (0.354) [e]	10.33 (0.483) [e]	-	99.9
21	7.10 (0.367)	15.95 (0.536)	68.99 (1.731)	91.8
	6.18 (0.344)	17.25 (0.874)	77.57 (1.835)	87.9
	6.65 (0.356)	17.60 (0.883)	70.54 (1.750)	-
22	8.08 (0.436)	16.73 (0.620)	77.83 (1.073)	105.3
	8.44 (0.446)	18.10 (0.645)	85.21 (1.120)	90.1
				76.8 [c]
	7.44 (0.270)	17.02 (0.626)	76.72 (1.065)	93.1
23	7.98 (0.309)	16.24 (0.438)	69.18 (0.898)	92.6
	7.98 (0.309)	17.30 (0.451)	70.74 (0.908)	96.9
	8.01 (0.309)	17.24 (0.451)	71.50 (0.791)	95.6

(continued)

See footnotes at end of table, page 18.

TABLE 1. (Continued)

Lab	Sample Uranium Concentration, (counting error), [a] pCi/l			Recovery [b] Percent
	1	2	3	
24	8.18 (0.602)	21.72 (0.921)	70.50 (1.761)	101.7
	6.23 (0.528)	21.99 (0.927)	69.43 (1.748)	91.6
	7.12 (0.563)	17.88 (0.837)	71.14 (1.769)	104.3
25	9.17 (0.623)	18.42 (0.863)	81.44 (1.784)	93.7
	7.47 (0.567)	16.52 (0.820)	83.91 (1.811)	93.0
	10.83 (0.672)	14.70 (0.776)	85.31 (1.826)	111.1

[a] S_u, counting uncertainty, pCi/l, one sigma.

[b] R, chemical recovery using a spiked (standard) sample, the average of the three replicates for each lab was used as factor (R) in calculating the uranium concentrations in samples 1, 2, and 3. The recoveries given here do not correspond to the sample data listed, but were determined independently with spiked samples by the test procedure.

[c] This chemical recovery factor was used only in calculating the uranium concentration for sample 3. The average of the other three values was used to calculate the uranium concentration of samples 1 and 2.

[d] Rejected by the ASTM Outlier Test.

[e] Rejected by t-test for significant differences (Youden and Steiner, 1975).

TABLE 2. URANIUM IN DRINKING WATER, PRECISION SUMMARY

Parameter [a]	Sample 1	Sample 2	Sample 3	Average
Y_j (pCi/l)	8.1 ± .4	17.4 ± .9	75.3 ± 3.9	
$\bar{X}_j$ (pCi/l)	7.9	17.9	76.8	
$S_{\bar{x}_j}$ (pCi/l)	0.76	2.39	4.6	
S_{r_j} (pCi/l)	1.15	1.44	6.39	
S_{L_j} (pCi/l)	0.37	2.24	2.83	
S_{R_j} (pCi/l)	1.21	2.66	6.98	
V_{r_j}%	14.6	8.1	8.3	10.3
V_{L_j}%	4.7	12.5	3.7	7.0
V_{R_j}%	15.3	14.9	9.1	13.1
$\bar{S}_{r_j}$ (pCi/l)	0.82	1.84	7.92	
$\bar{S}_{R_j}$ (pCi/l)	1.04	2.34	10.06	
I_{r_j} (pCi/l)	2.31	5.22	22.43	
I_{R_j} (pCi/l)	2.93	6.63	28.47	
p	18	17	18	

[a] Terms defined in text and the List of Abbreviations and Symbols.

TABLE 3. URANIUM IN DRINKING WATER, CELL AVERAGE ($\bar{X}_{ij}$) AND CELL STANDARD DEVIATION (S_{ij})

	Sample					
	1		2		3	
Lab	$\bar{X}_{ij}$	S_{ij}	$\bar{X}_{ij}$	S_{ij}	$\bar{X}_{ij}$	S_{ij}
1	9.1	0.38	21.6	1.77	84.1	8.91
2	8.7	1.56	21.2	3.34	84.3	9.22
3	7.6	0.49	13.0	0.85	78.7	4.54
4	8.4	0.58	15.0	0.58	74.9	2.18
5	7.9	0.28	16.8	1.06	76.4	2.57
7	6.5	0.51	18.4	0.59	77.1	4.98
8	7.7	3.55	22.0	0.94	73.6	7.89
9	7.5	0.70	17.5	1.06	72.4	3.80
10	9.0	0.18	17.6	0.21	69.8	3.08
11	7.4	0.70	15.8	1.19	79.2	12.07
12	7.6	0.80	0	0	77.3	0.50
14	8.3	0.67	17.7	1.60	79.5	14.19
18	7.7	1.19	18.9	1.14	77.4	3.61
21	6.6	0.46	16.9	0.87	72.4	4.57
22	8.0	0.51	17.3	0.72	79.9	4.61
23	8.0	0.02	16.9	0.60	70.5	1.18
24	7.2	0.98	20.5	2.30	70.4	0.86
25	9.2	1.68	16.5	1.86	83.6	1.96
$\bar{X}_j$	7.9		17.9		76.8	
S_{rj}	1.15		1.44		6.39	
U_j	0.65		0.82		3.62	
$S_{\bar{x}_j}$	0.76		2.39		4.65	

TABLE 4. URANIUM IN DRINKING WATER, DEVIATION OF LAB AVERAGE FROM GRAND AVERAGE (d_{ij}, pCi/l) AND PERCENT DEVIATION (% d_{ij})

Lab	Sample 1		Sample 2		Sample 3	
	d_{ij}	% d_{ij}	d_{ij}	% d_{ij}	d_{ij}	% d_{ij}
1	1.2	15.2	3.8	21.3	7.3	9.5
2	0.8	10.1	3.4	19.1	7.5	9.8
3	-0.3	3.8	-4.8	27.0	1.9	2.5
4	0.5	6.3	-2.8	15.7	-1.8	2.4
5	0.0	0.0	-1.0	5.6	-0.4	0.5
7	-1.4	17.7	0.6	3.4	0.3	0.4
8	-0.2	2.5	4.2	23.6	-3.2	4.2
9	-0.4	5.1	-0.3	1.7	-4.4	5.7
10	1.1	13.9	-0.2	1.1	-7.0	9.1
11	-0.5	6.3	-2.0	11.2	2.4	3.1
12	-0.3	3.8	0	0	0.5	0.6
14	0.4	5.1	-0.1	0.6	2.7	3.5
18	-0.2	2.5	1.1	6.2	0.6	0.8
21	-1.3	16.4	-0.9	5.0	-4.4	5.7
22	0.1	1.3	-0.5	2.8	3.1	4.0
23	0.1	1.3	-0.9	5.0	-6.3	8.2
24	0.7	8.9	2.7	15.2	-6.4	8.3
25	1.3	16.4	-1.3	7.3	6.8	8.8
$S_{\bar{x}_j}^2$	0.58		5.72		21.59	
$S_{\bar{x}_j}$	0.76		2.39		4.65	

TABLE 5. URANIUM IN DRINKING WATER, REDUCED DEVIATIONS, (e_{ij} [a], pCi/l)

Lab	Sample 1	Sample 2	Sample 3
1	1.9	4.6	2.0
2	1.2	4.1	2.1
3	-0.5	-6.0	0.5
4	0.9	-3.5	-0.5
5	0.0	-1.3	-0.1
7	-2.1	0.6	0.1
8	-0.2	5.0	-0.9
9	-0.6	-0.4	-1.2
10	1.7	-0.3	-1.9
11	-0.7	-2.5	0.7
12	-0.4	0	0.2
14	0.6	-0.2	0.8
18	-0.2	1.3	0.2
21	-1.9	-1.2	-1.2
22	0.1	-0.7	0.9
23	0.1	-1.2	-1.7
24	1.1	3.3	-1.8
25	1.9	-1.6	1.9
U_j	0.65	0.82	3.62
S_{r_j}	1.15	1.44	6.38

[a] Term defined in text and the List of Abbreviations and Symbols.

TABLE 6. URANIUM IN DRINKING WATER, RATIO OF LAB STANDARD DEVIATION TO POOLED STANDARD DEVIATION, k_{ij} [a]

Lab	Sample 1	Sample 2	Sample 3
1	0.33	1.23	1.40
2	1.35	2.31	1.44
3	0.42	0.59	0.71
4	0.51	0.40	0.34
5	0.24	0.74	0.40
7	0.44	0.41	0.78
8	3.08	0.65	1.24
9	0.60	0.74	0.60
10	0.16	0.15	0.48
11	0.61	0.83	1.89
12	0.70	-	0.08
14	0.58	1.11	2.22
18	1.04	0.79	0.56
21	0.40	0.60	0.72
22	0.44	0.50	0.72
23	0.01	0.41	0.18
24	0.85	1.59	0.14
25	1.46	1.29	0.31

[a] Term defined in text and the List of Abbreviations and Symbols.

k_c = 2.06 for 18 labs and 3 replicates

TABLE 7. URANIUM IN WATER, ACCURACY INDEX (A_j) AND BIAS (t_j)

Parameter [a]	Sample 1	Sample 2	Sample 3	Average
Y_j (pCi/l)	8.1 ± .4	17.4 ± .9	75.3 ± 3.9	
$\bar{X}_j$ (pCi/l)	7.9	17.9	76.8	
A_j %	98.0	102.6	101.9	100.8
S_{x_j} (pCi/l)	0.76	2.39	4.65	
t_j	-0.90	0.79	1.30	
t_c	2.10	2.11	2.10	
p	18	17	18	

[a] Terms defined in text and the List of Abbreviations and Symbols.

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APPENDIX A

LABORATORIES PARTICIPATING IN THE URANIUM IN DRINKING WATER COLLABORATIVE STUDY

Alabama State Department of Public Health
Montgomery, Alabama

Arkansas Department of Health
Little Rock, Arkansas

California Department of Health Services
Sanitation and Radiation Laboratory
Berkeley, California

Florida Department of Health and Rehabilitative Services
Radiological Health Services
Orlando, Florida

Hazen Research, Inc.
Golden, Colorado

Massachusetts Department of Environmental Quality Engineering
Lawrence Experiment Station
Lawrence, Massachusetts

Michigan Department of Public Health
Division of Radiological Health
Lansing, Michigan

New Hampshire Water Supply and Pollution Control Commission
Concord, New Hampshire

Oregon Department of Human Resources
Health Division Radiation Section
Portland, Oregon

Orlando Laboratories, Inc.
Orlando, Florida

Rockwell Hanford Operations
Richland, Washington

U. S. Army Environmental Hygiene Agency
Aberdeen Proving Ground, Maryland

U. S. Environmental Protection Agency
Environmental Monitoring and Support Laboratory
Cincinnati, Ohio

U. S. Environmental Protection Agency
Eastern Environmental Radiation Facility
Montgomery, Alabama

U. S. Food and Drug Administration
Winchester Engineering and Analytical Center
Winchester, Massachusetts

University of Pittsburgh
Graduate School of Public Health
Pittsburgh, Pennsylvania

Union Carbide Corporation
Nuclear Division
Oak Ridge, Tennessee

Union Carbide Corporation
Nuclear Division, Analytical Dept.
Paducah, Kentucky

Washington State Department of Social and Health Services
Seattle, Washington

APPENDIX B

URANIUM IN DRINKING WATER-RADIOCHEMICAL METHOD
METHOD 908.0
MAY 8, 1980

1. Scope and Application

1.1 This method covers the measurement of total uranium alpha particle activity in drinking water. Most drinking water sources, especially ground water sources, contain soluble carbonates and bicarbonates which complex and keep uranium in the water in solution.

1.2 Uranium isotopic abundances in drinking water sources are apt to be present in ratios different from the ratios in the deposits from which the uranium entered the water sources. The two predominant natural alpha emitting isotopes of uranium are uranium-234 and uranium-238. Uranium-238 is the predominant mass abundant isotope; greater than 99% compared to about 0.006% for uranium-234. However, uranium-234 has a specific activity for alpha particle emission that is 1.8×10^4 times greater than that of uranium-238. For an equilibrium condition, the activity of the uranium-234 is equal to that of the uranium-238. Therefore, the uranium mass concentration in water is not related to the alpha particle activity of the water.

1.3 The Drinking Water Regulations under the Safe Drinking Water Act, PL 93-523, require a measurement of uranium for drinking water samples that have a gross alpha activity greater than 15 pCi/l. A mass uranium concentration measurement of a water sample cannot be converted to uranium alpha activity without first analyzing for isotopic abundances. Therefore, a method such as this one is needed to determine the total uranium alpha activity of the sample, without doing an isotopic uranium analysis.

2. Summary of Method

2.1 The water sample is acidified by adding HCl and the sample is boiled to eliminate carbonate and bicarbonate ions. Uranium is coprecipitated with ferric hydroxide and separated from the sample. The uranium is then separated from other radionuclides which were carried down with the ferric hydroxide by dissolving the hydroxide precipitate in 8N HCl; putting the solution through an anion exchange column; washing the column with 8N HCl; and finally, eluting the uranium with 0.1N HCl. The uranium eluate is evaporated and the uranium chemical form is converted to nitrate. The residue is transferred to a stainless steel planchet, dried, flamed, and counted for alpha particle activity.

2.2 Uranium recovery is determined with blank samples spiked with known amounts of uranium and taken through the procedure as a regular sample.

2.3 Counting efficiency is determined by transferring measured aliquots of a uranium standard to a planchet, diluting with 6-8 ml of a 1 mg/ml HIO_3 solution in 4N HNO_3, evaporating to dryness, flaming the planchet, and counting in an alpha counter.

3. Sample Handling and Preservation

3.1 Although carbonate ions in a water sample will help to keep uranium in solution, the addition of extra carbonate or bicarbonate ions to the sample as a preservative is not recommended because an increased carbonate concentration in the sample may cause some precipitation. Therefore, it is recommended that samples be preserved with HCl to pH 2 at the time of collection.

3.2 A sample size of, at least, 1 liter should be collected for uranium analysis.

4. Interferences

4.1 The only alpha-emitting radionuclide that may come through the chemistry and cause interference would be protactinium-231. However, protactinium-231 results from the decay of uranium-235, a low abundance natural isotope of uranium, and would therefore cause only a very small interference.

4.2 Since uranium is a naturally occuring radionuclide, reagents must be checked for uranium contamination by analyzing a complete reagent blank by the same procedure as used for the samples.

5. Apparatus

5.1 Gas-flow proportional counting system or

5.2 Scintillation detection system.

5.3 Electric hot plate.

5.4 Ion exchange column: approximately 13 mm (i.d.) x 150 mm long with a 100 ml reservoir.

5.5 Stainless steel counting planchets, 2 inch diameter by 1/4 inch deep.

5.6 Millipore filter apparatus, 47 mm.

6. Reagents

6.1 All chemicals should be of reagent grade, or equivalent, whenever they are commercially available.

6.2 Ammonium hydroxide, 6N: Mix 2 volumes 15N NH_4OH (conc.) with 3 volumes of water (carbonate-free).

6.3 Anion exchange resin - Strongly basic, styrene, quaternary ammonium salt, 4% crosslinked, 100-200 mesh, chloride form (such as Dowex 1x4, or equivalent).

6.4 Ferric chloride carrier, 20 mg Fe^{+3}/ml: Dissolve 9.6 g of $FeCl_3 .6 H_2O$ in 100 ml of 0.5N HCl.

6.5 Hydriodic acid: HI (conc.), sp. gr. 1.5, 47%.

6.6 Hydrochloric acid, 12N: HCl (conc.), sp. gr. 1.19, 37.2%.

6.7 Hydrochloric acid, 8N: Mix 2 volumes 12N HCl (conc.) with 1 volume of water.

6.8 Hydrochloric acid, 6N: Mix 1 volume 12N HCl (conc.) with 1 volume of water.

6.9 Hydrochloric acid, 0.1N: Mix 1 volume 0.5N HCl with 4 volumes of water.

6.10 Iodic acid, 1 mg/ml: Dissolve 100 mg HIO in 100 ml 4N HNO_3.

6.11 Nitric acid, 16N: HNO_3 (conc.), sp. gr. 1.42, 70.4%

6.12 Nitric acid, 4N: Mix 1 volume 16N HNO_3 (conc.) with 3 volumes of water.

6.13 Sodium hydrogen sulfite, 1% in HCl: Dissolve 1 g $NaHSO_3$ in 100 ml 6N HCl.

7. Calibrations

7.1 Determine a counting efficiency (E), for known amount of standard uranium (about 1000 dpm) evaporated from a 6-8 ml volume of a 1 mg/ml HIO_3 solution in a 2-inch planchet. If the standard solution is an HCl solution, then aliquot portions of that solution must be converted to nitrate/HNO_3 solutions, eliminating all chloride ions from the solutions. This can be done by three successive evaporations after adding 5 ml portions of 16N HNO_3 to aliquot portions of the standard in small beakers (avoiding dry baking of the evaporated residue). The final solutions of the standard aliquots are made by adding 2 ml 4N HNO_3 solution to the third evaporated residues. Transfer the uranium standard aliquot solutions to 2 inch diameter stainless steel planchets.

Complete the transfer by rinsing the beakers two times with 2 ml portions of 4N HNO_3 and evaporate to dryness. Flame the planchets and count for, at least, 50 minutes for alpha particle activity. A reagent blank should be run along with the standard aliquots and should be alpha counted.

$$\text{Efficiency, cpm/dpm, (E)} = \frac{A - B'}{C} \qquad \text{Eq. 1}$$

where:
A = gross cpm for standard
B' = cpm for instrument background
C = dpm of standard used

7.2 A uranium recovery factor R, is determined by the following procedure: Spike one liter tap water samples with aliquots of uranium standard solution (500-1000 dpm per sample). Take these spiked samples and a tap water blank through the entire procedure and count the separated and evaporated uranium for alpha particle activity.

$$\text{Recovery factor, (R)} = \frac{(F - B)}{C\ E} \qquad \text{Eq. 2}$$

where:
C = dpm of uranium standard added
F = gross cpm of spiked sample
B = cpm of reagent blank
E = efficiency factor, cpm/dpm

8. Procedure

8.1 Measure the volume of approximately one liter of the water sample to be analyzed.

8.1.2 If the sample has not been acidified, add 5 ml 12N HCl and 1 ml ferric chloride carrier.

8.1.3 Mix the sample completely and use pH paper to check the hydrogen-ion concentration. If the pH is >1, add 12N HCl until it reaches this value.

8.1.4 Cover with a watch glass and heat the water sample to boiling for 20 minutes.

8.1.5 The pH must be checked again after boiling and if it is >1, 12N HCl must be added to bring the pH back to 1.

8.1.6 While the sample is still boiling, gently add 6N NH_4OH to the sample from a polyethylene squeeze bottle with the bottle delivery tube inserted between the watch glass and the pouring lip of the beaker. The boiling action of the sample provides sufficient stirring action. Add 6N NH_4OH until turbidity persists while boiling continues; then add an

additional 10 ml, (estimated addition from the squeeze bottle).

8.1.7 Continue to boil the sample for 10 minutes more; then set it aside for 30 minutes to cool and settle.

8.1.8 After the sample has settled sufficiently, decant and filter the supernate through a 47 mm 0.45 micron membrane filter, using the larger millipore filtering apparatus.

8.1.9 Slurry the remaining precipitate, transfer to the filtering apparatus and filter with suction.

8.1.10 Place the filtering apparatus over a clean 250 ml filtering flask, add 25 ml 8N HCl to dissolve the precipitate, and filter the solution.

8.1.11 Add another 25 ml 8N HCl to wash the filter, and then filter.

8.1.12 Transfer solution to the 100 ml reservoir of the ion exchange column.

8.1.13 Rinse the side arm filtering flask twice with 25 ml portions of 8N HCl. Combine in the ion exchange reservoir.

8.2 Anion Exchange Separation

8.2.1 Prepare the column by slurrying the anion exchange resin with 8N HCl and pouring it onto a column about 13 mm inside diameter. The height of the resin bed should be about 80 mm.

8.2.2 Pass the sample solution through the anion exchange resin column at a flow rate not to exceed 5 ml/minute.

8.2.3 After the sample has passed through the column, elute the iron, (and plutonium if present), with 6 column volumes of 8N HCl containing 1 ml 47% HI per 9 ml of 8N HCl (freshly prepared).

8.2.4 Wash the column with an additional two column volumes of 8N HCl.

8.2.5 Elute the uranium with six column volumes of 0.1N HCl.

8.2.6 Evaporate the acid eluate to near dryness and convert the residue salts to nitrates by three successive treatments with 5 ml portions of 16N HNO_3, evaporating to near dryness each time.

8.2.7 Dissolve the residue (may be very little visible residue) in 2 ml 4N HNO_3.

8.2.8 Transfer the residue solution, using a Pasteur pipet, to a marked planchet, and complete the transfer by rinsing the sample beaker three times with 2 ml portions of 4N HNO_3.

8.2.9 Evaporate the contents in the planchet to dryness, flame to remove traces of HIO_3, cool, and count for alpha particle activity.

8.3 Column Regeneration

8.3.1 Pass three column volumes of 1% $NaHSO_3$ in 6N HCl through the column.

8.3.2 Pass six column volumes of 6N HCl through the column.

8.3.3 Pass three column volumes of water through the column.

8.3.4 Pass six column volumes of 8N HCl through the column to equilibrate and ready the resin for the next set of samples.

9. Calculations

$$\text{Uranium alpha activity, pCi/l} = \frac{(S - B) \times 1000}{2.22 \times E \; R \; V} \qquad \text{Eq. 3}$$

where:

S = gross cpm for sample
B = cpm of reagent blank
V = volume of sample used, ml
E = efficiency, cpm/dpm
R = recovery factor
2.22 = conversion factor for dpm/pCi

10. Precision and Accuracy

In a single laboratory test of this method, a stock uranium solution was prepared using tap water and spiked with an NBS uranium standard. The calculated concentration was 26.7 pCi/l. This stock solution was acidified with HCl as a preservative. Nine 1-liter aliquots were withdrawn and the procedure tested. Individual results were 22.4, 22.5, 24.0, 25.9, 26.9, 26.5, 24.6, 25.7 and 23.9 pCi/l. The average concentration was 24.7 pCi/l with a standard deviation of 1.7 pCi/l. From these data, the method shows a negative 7.4% bias and a precision of ±6.7% without the correction of the recovery factor.

REFERENCES

1. Bishop, C. T., et al. "Radiometric Method for the Determination of Uranium in Water", EPA 600/7-79-093, EMSL-LV, April 1979.

2. Edwards, K. W. "Isotopic Analysis of Uranium in Natural Waters by Alpha Spectrometry", Radiochemical Analysis of Water, Geological Survey Water - Supply Paper 1696-F, U. S. Government Printing Office, Washington, D.C., 1968.

APPENDIX C

URANIUM IN DRINKING WATER
COLLABORATIVE TEST - MAY, 1980
DATA SHEET

LABORATORY:

CONTACT PERSON:

DATE:

Sample ID	Vol (ml)	Gross[a] Counts	Counting Time (min.)	Counter Bkg (c/m)	Bkg Counting Time (min.)	Uranium Alpha Activity[b] pCi/l (In sample or blank)
1 a						
1 b						
1 c						
2 a						
2 b						
2 c						
3 a						
3 b						
3 c						
Blank a						
Blank b						
Blank c						

Recovery Factor (R), Determinations in % _____

Average of (R) _____%

Counting Efficiency (E), Determinations in % _____

Average of (E) _____%

[a]Total counts including background.

[b]As calculated from the equation in section 9 of the procedure. For the purpose of this collaborative study, the reagent blank B is defined as the cpm observed in one liter of your drinking water including the counter background.

PLEASE SEND RESULTS TO C. A. PHILLIPS, MONSANTO RESEARCH CORPORATION, MOUND FACILITY, MIAMISBURG, OH 45342, BY JULY 18, 1980. FTS 774-3228 (or 3927) or 513-865-3228 (or 3927)

APPENDIX D

COLLABORATIVE STUDY INSTRUCTIONS - URANIUM IN DRINKING WATER
(May 1980)

1. Use the procedure "Uranium in Drinking Water - Radiochemical Method, Method 908.0" dated May 1980.

2. If you have not used a procedure similar to the one enclosed, it would be advisable to analyze a few known samples, before analyzing the test samples.

3. If you do not have the ion exchange resin, or other reagents needed for the analysis of the test samples, Mound Facility will furnish them if you desire.

4. Use care in opening the glass ampoules which contain the sample concentrates and are labeled uranium concentrate 1, 2 and 3. Each ampoule contains a solution of known concentration of uranium-238 + uranium-234 in 0.5M HCl. The analyst should pipet exactly 5 ml of the concentrate and dilute this volume to one liter with drinking water in a volumetric flask. Each sample should be prepared in triplicate from each uranium concentrate.

5. The diluted one-liter samples just prepared are the samples to be analyzed. For example, the 5 ml aliquot of uranium concentrate #1 diluted to one liter with drinking water is sample #1. The analyst should therefore calculate the concentration of this diluted sample.

6. The above samples are listed as 1, 2, 3 on the enclosed Uranium In Drinking Water Collaborative Test May 1980 Data Sheet.

7. A uranium standard of known concentration has been sent to you from the Environmental Protection Agency in Las Vegas. This standard should be used to determine your counting efficiency and uranium recovery factor.

8. Additional amounts of any uranium concentrates are available if a sample is spilled, or an obviously incorrect uranium concentration is obtained, etc.

9. Sample concentrations may be below 15 pCi/l. Reagent blanks of your drinking water should be made in your laboratory to be certain that they are not a problem at this uranium concentration.

10. The reagent blank (B) for the purpose of this collaborative study is defined as the cpm observed in one liter of your drinking water including the counter background. (Ordinarily, the reagent blank is determined using distilled, deionized water.)

11. We are requesting that uranium concentrations in all samples, counter efficiency determinations (E), recovery factors (R), and drinking water blanks be determined in triplicate.

12. All samples should be counted for at least 50 minutes. Longer counting times are advisable for blanks and any low-level sample.

13. Individual counting data is requested so that the counting statistics error can be resolved from other errors.

APPENDIX E

QUESTIONNAIRE SUMMARY
QUESTIONNAIRE ON COLLABORATIVE STUDY
OF URANIUM IN DRINKING WATER, MAY, 1980

Laboratory _____ Contact _____

1. Did you make a blank correction?

   Yes 19 No ____

2. When you pipeted the tracer, was the volume of the pipet calibrated?

   Yes 16 No 3

3. Did you regenerate the anion exchange resin?

   Yes 16 No 3

4. Did you deviate considerably from any part of the procedure?

   Yes ____ No 19

   If so, what were these deviations? (answer on other side)

5. Do you believe that this would be a good reference method for uranium in drinking water?

   Yes 15 No 2*

6. Any other comments that you might have would be appreciated.

*Two more were undecided.

APPENDIX F

COMMENTS FROM PARTICIPANTS IN COLLABORATIVE STUDY

1. The general procedure appears to be a quick method for total uranium determination. The sample loss during handling appears to be minimal, and the analytical procedure appears much simpler than the fluorometric procedure.

2. The procedure for calibration assumes that the addition of iodic acid to the standard duplicates the final composition of the ion exchange eluate. The residue on a planchet after the ion exchange procedure was visibly less than the amount of iodic acid visible on a planchet prepared according to the calibration procedure. Thus, the addition of iodic acid is not felt to be an appropriate method of correcting for self-absorption and counting efficiency simultaneously. The counting efficiency determined by the calibration procedure is possibly too low and does not allow for any variability in the amount of residue.

3. The quantitative transfer of the uranium eluant from the beaker to the planchet prior to counting is questionable. In addition, "creeping" of the sample on the side of the planchet was observed thereby introducing some uncertainty in counting efficiency.

4. The procedure should specify new anion exchange resin rather than regenerating resin.

5. For every set of samples, analyze a spiked sample and one of the samples in duplicate to check the recovery factor.

6. The use of the term "column volume" would possibly be confusing to a technician. In the entire procedure, column volume should be expressed as milliliters.

7. A better estimate of the counting efficiency and a self-absorption factor can be made by determining the "weightless" counting efficiency and developing a self-absorption curve to use with the procedure. The self-absorption curve can be made using iodic acid to increase the mass per unit area on the planchet as the same amount of uranium is added to each planchet. The flaming procedure is not used as this weight must be accurately determined, and the flaming procedure could create variability in the planchet weight.

   The recovery factor would require weighing the planchet before and after the residue has been dried on it and using the net mass per unit area to find the self-absorption factor.

The formula would be:

$$R = \frac{(F - B)}{C\ E\ A} \qquad \text{Eq. 4}$$

where: F = gross count per minute of spiked sample
B = counts per minute of reagent blank
C = disintergrations per minute of uranium standard added
E = counting efficiency = cpm weightless std./dpm weightless std.
A = self-absorption factor = cpm of std. of this mass/unit/area/cpm of weightless std.

$$\text{Uranium alpha activity, pCi/l} = \frac{(S - B) \times 1000}{2.22 \times E \times A \times V \times R} \qquad \text{Eq. 5}$$

where: S = gross cpm for sample
B = cpm of reagent
V = volume of sample used, ml
E = efficiency, cpm/dpm
A = self-absorption factor based on mass/unit area (unitless)
2.22 = conversion factor for dpm/pCi
R = recovery factor

8. In step 8.2.6 by adding 16M HNO_3 to a small volume of the evaporated uranium eluant, the iodate would be reduced to the free iodine, thereby, eliminating the iodate on the counting planchet.

9. The procedure should call for the fresh preparation of NH_4OH for each analysis which would preclude the formation of the CO_3 ion.

10. Uranium yields will vary considerably depending on the amount of dissolved solids in the water sample.

11. Some participants believed the method was good and easy to follow, while others believed the method was time consuming, complex, and would be too expensive for a routine method.

12. This method should be an alternative method of a fluorometric or alpha spectrometric method.